Argonne NATIONAL LABORATORY

ANL/NE-15/31

Plant-Scale Concentration Column Designs for SHINE Target Solution Utilizing AG 1 Anion Exchange Resin

Nuclear Engineering Division

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Plant-Scale Concentration Column Designs for SHINE Target Solution Utilizing AG 1 Anion Exchange Resin

by
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PLANT-SCALE CONCENTRATION COLUMN DESIGNS FOR SHINE TARGET SOLUTION UTILIZING AG 1 ANION EXCHANGE RESIN

1 INTRODUCTION

Argonne is assisting SHINE Medical Technologies (SHINE) in their efforts to develop SHINE, an accelerator-driven process that will utilize a uranyl-sulfate solution for the production of fission product Mo-99. An integral part of the process is the development of a column for the separation and recovery of Mo-99, followed by a concentration column to reduce the product volume from 15–25 L to <1 L. Argonne has collected data from batch studies and breakthrough column experiments to utilize the VERSE (Versatile Reaction Separation) simulation program (Purdue University) to design plant-scale product recovery and concentration processes.

For typical conditions for recovery of Mo-99, 260 L of 130 g-U/L uranyl-sulfate solution is loaded on a 12 × 13 cm Sachtopore S110 column in 2 hr (Youker 2012). The product is stripped with 23.5 L of 0.1 M NaOH, producing a 0.0234 mM Mo solution. The 23.5 L of Mo-product solution volume is too large for subsequent Cintichem purification process and is further reduced using a concentration column (Stepinski et al. 2012). In this process, the alkaline Mo-product solution is acidified to pH 2 using 8 M HNO_3, and subsequently loaded on a 4 × 1.5 cm Sachtopore S40 column in 1 h. The product is stripped from the S40 concentration column with 302 mL of 1 M NH_4OH, which is subsequently brought to dryness and taken up in 1 M HNO_3 for the low-enriched uranium (LEU) Modified Cintichem purification process. The pressure drop, ΔP, constraint for both columns is 0.8 atm because the solution transfer system is based on the use of vacuum/gravity; therefore, pressure loss is limited to <1 atm.

The acidification of the Mo-99 product prior to loading on a concentration column and reduction of the Mo-99 to dryness prior to Cintichem adds about 3 h to processing. A loss of 3 h in processing Mo-99 is significant; about 1% per hr of Mo-99 activity is lost to decay. Therefore, lowering of processing time is important.

AG 1 resins are strongly basic anion exchangers capable of exchanging anions of acidic, basic, and neutral salts and ampholytes on the basic side of their isoelectric point (pI) (Bio-Rad undated a,b). They are used in a variety of applications such as metal separations, enzyme assays, and peptide, protein, and nucleic acid separations. These basic anion exchange resins are available in analytical grade. The resins have been exhaustively sized, purified, and converted to make them suitable for accurate and reproducible separations. The functionality of the AG 1 resins is provided by quaternary ammonium functional groups attached to the styrene divinylbenzene copolymer lattice. The amount of resin crosslinkage determines the bead pore size. Therefore, a resin with a lower percentage of crosslinkage has a more open structure that is permeable to higher molecular-weight substances than a highly crosslinked resin. It also has a lower physical resistance to shrinking and swelling, so it absorbs more water and swells to a larger wet diameter than a highly crosslinked resin of equivalent dry diameter. Therefore, the higher crosslinked resins, particularly AG 1-X8 (8% crosslinked) resin, is used for sorption, exchange, and separation of low-molecular-weight inorganic anions.

AG 1 resins are supplied in chloride, acetate, formate, and hydroxide forms (Bio-Rad undated a,b). The hydroxide form can be considered the most activated; the selectivity for the hydroxide, acetate, formate and chloride is 1, 3.2, 4.6 and 22, respectively. The resins are thermally stable and resistant to solvents (alcohols, hydrocarbons, etc.), reducing agents, and oxidizing agents. AG 1 hydroxide form is thermally stable to 50°C, and the acetate, formate, and chloride forms are stable to 150°C.

The mechanism of sorption on AG 1 is ion exchange, where ions are adsorbed by electrostatic forces and the counter ions on the resin are replaced by ions from the solution. Neutral species and cations do not interact with AG 1 resin. AG 1 resin is available in several particle size ranges: 45–106, 106–180, 180–425, and 300–1200 μm wet bead size. The larger resin particle sizes allow higher flowrates relative to pressure drop; however, because the solute spends a relatively larger amount time in the inter-particle space relative to the intraparticle space, the mass transfer zone (the spreading wave of the solute) increases, resulting in a larger overall column. The smaller particle size resins are ideal for high-resolution analytical separations. Therefore, for most efficient column design, it is important to choose the smallest particle size resin within the pressure drop constraint.

In this work, we examine the use of AG 1 resin for concentrating Mo-99 recovery column product from 23.5 L to <1 L. The VERSE simulation program was used in this work to design the Mo concentration column using AG 1 resin. The objective is to design a column process that provides an acidic feed solution for the LEU-Modified Cintichem process, thereby eliminating the need to evaporate ammonium solution and re-dissolve Mo in 1 M HNO_3 solution. The objective of the concentration column is also to provide a product volume that is <1 L. The VERSE model and related simulations were developed by Wang and associates in 1991 (Berninger 1991). The general VERSE model takes into account detailed mass-transfer effects (axial dispersion, film mass transfer, intra-particle pore, and surface diffusion), adsorption and desorption rates, and any chemical reactions in the mobile phase or in the solid phase during the separation. A variety of batch and chromatography processes can be simulated by determining the initial and boundary conditions. When the simulations are complete, effluent histories and dynamic column profiles are created. These figures and animations are important in understanding separation mechanisms and improving conditions.

AG-1 anion exchange resin strongly sorbs MoO_4^{2-}, I^-, and IO_3^- from alkaline media. Replacement of titania sorbent with AG 1 anion exchange resin provides two other benefits. First, iodine decontamination is challenging to the in the LEU-Modified Cintichem process, and its removal during the prior Mo-product-concentration step would decrease the technical risk of radioiodine contamination of the final Mo product. Second, it provides an opportunity to capture and recover I-131 for commercial purposes if the radioiodine is recovered from the resin in a separate strip following Mo stripping. Molybdenum can be removed from the column using nitric acid; other iodine species and iodate will be removed during prior wash steps. Most of the iodide will remain on the column as molybdenum is stripped. The iodide can subsequently be removed with more aggressive stripping agents. This approach is currently used in Argentina, where anion exchange is used to recover and purify Mo-99, while I^- is collected for sale.

2 EXPERIMENTAL

2.1 BATCH STUDIES

AG 1 X8 was obtained from Bio-Rad, (Hercules, CA). Uptake of Mo from 0.1 M NaOH solutions was determined by equilibrating 1 mL of 0.002–1 mM Mo, added as Na_2MoO_4, with a known amount (10 ± 1 mg) of AG 1 X8 for 20 minutes at room temperature using a vortexing mixer. Mo uptake was also measured at 80°C using a shaking thermostated bath by equilibrating 0.1–23 mM Mo in 0.1 M NaOH solutions with AG 1 X8. After equilibration, the solutions were withdrawn and filtered using a syringe fitted with a 0.22-μm pore size PVDF (polyvinylidene fluoride) membrane filter.

2.2 PREPARATION OF Mo-99 SPIKE SOLUTION

Mo-99 was obtained from a 1-Ci Tc-99m generator (Lantheus, Billerica, MA). Mo-99 is removed from the generator by stripping with 0.1 M NaOH.

2.3 COUNTING OF Mo-99

The amount of activity in the aqueous samples is determined using a Perkin Elmer 1480 Wizard 3-inch NaI Gamma Counter in the 700–900 keV window.

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3 RESULTS AND DISCUSSION

AG 1-X8 was selected for adsorbing and concentrating Mo from the recovery column-strip solution. It has a higher physical resistance to shrinking and swelling, so it absorbs less water and swells to a smaller wet diameter than a lower crosslinked resin of equivalent dry diameter. The 200–400 mesh (45–106 μm) wet bead size was selected for this application because it allows column design within the 0.8 atm ΔP constraint but also provides high resolution and lower spreading of the mass transfer zone. Ion exchange on organic resins is kinetically superior to adsorption on inorganic sorbents such as titania, and therefore can result in shorter mass transfer zone and smaller column.

3.1 BATCH STUDIES AND ESTIMATION OF THE EFFECTIVE ISOTHERM PARAMETERS OF Mo IN 0.1 M NaOH SOLUTION

When sorption rates are higher than the controlling mass transfer rate, local equilibrium can be achieved between the solid and pore phases. Under such conditions, the solid phase concentrations are related to pore-phase concentrations by an equilibrium isotherm. The Langmuir model is tested for the sorption of Mo in this study:

$$q_i = \frac{a_i C_i}{1 + b_i C_i} \qquad \text{Eq. 1}$$

where q_i is the amount of species i sorbed on the column packing and equilibrated with the concentration in mobile phase, C_i. In this study, both q_i (mmol/L sorbent) and C_i (mmol/L) of the Mo isotherm is described on volume basis assuming 0.82 g/mL wet packing density of AG 1-X8 sorbent. The density was determined by placing a known mass of sorbent in an Omnifit column that was then packed using an ÄKTA purifier 100 Lab-Scale Chromatography System's sample pump, and then by measuring the volume of the sorbent in the packed column.

AG 1-X8 was evaluated for recovery of Mo from 0.1 M NaOH (Figure 1). The data from batch equilibrium experiments were used to estimate the effective Mo isotherm parameters for AG 1-X8 resin. Langmuir isotherm parameters were fitted using Origin 8.5.1. The Langmuir isotherm model parameter in 0.1 M NaOH is $a = 5274$, $b = 9.59$ mM^{-1} (Figure 1).

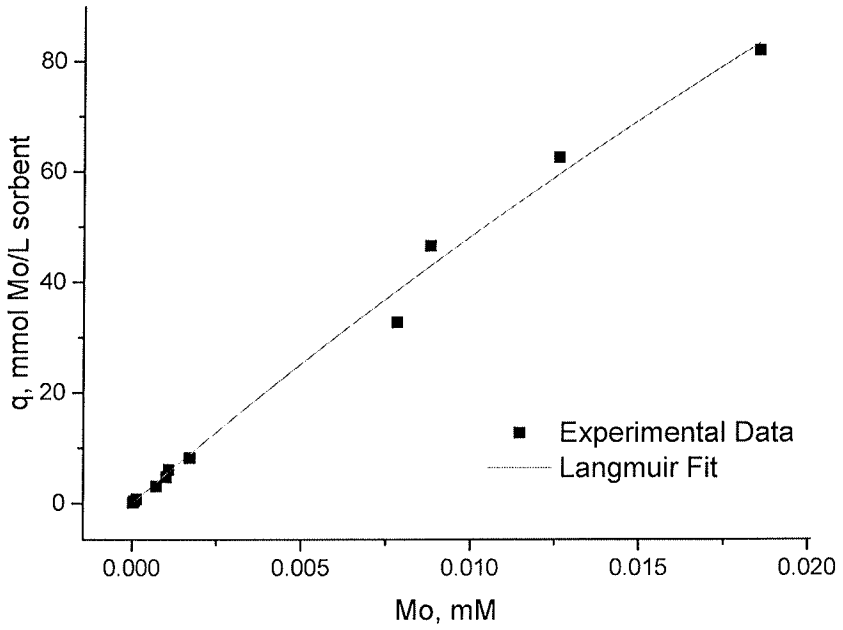

FIGURE 1 Langmuir Isotherm for Uptake of Mo on AG 1-X 8 Resin from 0.1 M NaOH Solution at Room Temperature

The isotherm parameters for AG 1-X8 for recovery of Mo from 0.1 M NaOH were also measured at 80°C (Figure 2). The data from batch equilibrium experiments were used to estimate the effective Mo isotherm parameters for AG 1-X8 resin. Langmuir isotherm parameters were fitted using Origin 8.5.1. The Langmuir isotherm model parameter at 80°C were determined to be $a = 844$, $b = 1.3\ mM^{-1}$. The Langmuir adsorption constant $a = 844$ at 80°C is significantly lower than $a = 5274$ at 25°C. The adsorption constant at 80°C was expected to be higher than that obtained at room temperature. There are several reason why the adsorption constant at 80°C is lower than at room temperature: (1) the shaking bath used in this experiment provided gentle mixing compared to the robust vortexing used for the room temperature experiments or (2) AG 1-X8 resin in OH^- form is degraded, as it is specified to be stable to 50°C. Consequently, for the concentration column designs, room temperature conditions were used.

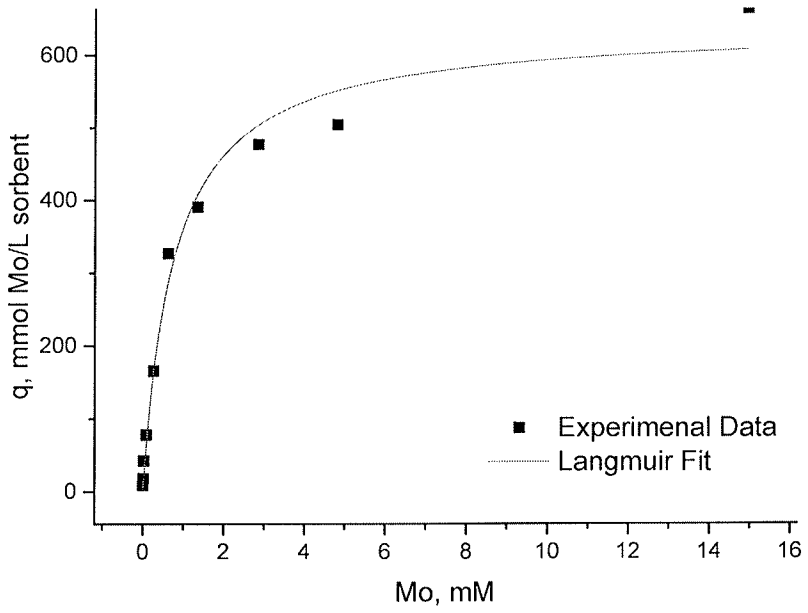

FIGURE 2 Langmuir Isotherm for Uptake of Mo on AG 1 X-8 Resin from 0.1 M NaOH Solution at 80°C

Stripping of Mo from AG 1-X8 was tested using 0.1 M and 1 M HNO_3. Uptake in 0.1 M HNO_3 was determined to be $K_d = 154$; however, for 1 M HNO_3 Mo solution activity before and after contact with resin could not be distinguished, which suggests that stripping with 1 M HNO_3 is very efficient.

3.2 COLUMN DESIGN PARAMETERS

The intrinsic mass transfer parameters and physical properties of 0.1 M NaOH given below were input into VERSE to design the plant-scale concentration column.

1. The Brownian diffusivity (D_∞) value of $HMoO_4^-$ in water at 25°C (viscosity = 0.8851 cp) was reported to be 8.3×10^{-4} cm^2/min (Xu and Pruess 2001; Marcus 1997).

2. The density of a 0.1 M NaOH solution 25°C was assumed to be the same as that of water: 0.997 g/mL.

3. Viscosity of a 0.1 M $NaNO_3$ solution at 25°C was also assumed to be the same as that of water: 0.89 cp.

4. *Eb*, axial dispersion estimated using Chung and Wen (1968) correlation.

5. *kf*, mass transfer coefficient estimated using Wilson and Geankoplis (1966).

6. AG 1-X8 sorbent intra-particle voidage for packed beds was empirically estimated, $\varepsilon_b = 0.35$ and porosity was calculated assuming total void fraction $\varepsilon_t = 0.6$, then $\varepsilon_p = (\varepsilon_t - \varepsilon_b)/(1-\varepsilon_b) = 0.40$.

3.3 INTRAPARTICLE DIFFUSIVITY

Mo intraparticle diffusivity, D_p, for AG1-X8 was empirically estimated to be approaching Mo Brownian diffusivity. It is well known that uptake on organic resins is kinetically robust. The ratio of Mo solution diffusivity, D_∞, to intraparticle diffusivity on titania sorbent S40 from 0.1 M NaOH solution was determined to be $D_\infty/D_p = 30$ (Stepinski et al. 2012). In contrast, the Mo intraparticle diffusivity on ABEC (Eichrom Industries, Lisle, IL) organic resin was observed to be very close to Mo solution diffusivity (Stepinski 2014). Consequently, the designs of the concentration column using AG 1-X8 were based on $D_\infty/D_p = 1$ and $D_\infty/D_p = 3$. The target Mo capture for the concentration column designs is 99% and 99.9%. The mass transfer zone (MTZ) was simulated using VERSE; it is the dimensionless length of the column where the concentration of Mo is between 0.1% and 99% of the Mo feed concentration for the 99% column designs, and the concentration of Mo is between 0.1% and 99.9% for the 99.9% column designs.

3.4 PRESSURE DROP CALCULATIONS

Pressure drop, ΔP, within the sorbent bed is calculated using the Ergun equation, where ε_b is inter-particle void fraction, μ is solution viscosity, ρ is solution density, d_p is diameter of sorbent particle, u_s is superficial velocity and L is length of the column:

$$\Delta P = L \times \left[150 \frac{(1-\varepsilon_b)^2}{{\varepsilon_b}^3} \frac{\mu u_s}{{d_p}^2} + 1.75 \frac{(1-\varepsilon_b)}{{\varepsilon_b}^3} \frac{\rho {u_s}^2}{d_p}\right] \quad \text{Eq. 2}$$

Column designs are chosen based on maximum ΔP = 0.8 atm.

3.5 COLUMN DESIGNS

Column designs utilizing AG 1-X8 were developed for concentrating Mo product recovered from 130 gU/L uranyl sulfate solutions and stripped with 0.1 M NaOH. The concentration column process was designed utilizing loading time of 1 h, as for the concentration column process using titania S40. Column lengths are chosen by rounding up the MTZ length to the nearest 0.25 cm.

TABLE 1 Concentration Column Designs for 99.9% Mo Capture Assuming $D_\infty/D_p = 1$

Column	Velocity	$MTZ_{0.1\%}$	Column	Column	Sorbent	ΔP (atm)	Strip

ID (cm)	(cm/min)	(cm)	Length (cm)	Volume (mL)	Weight (g)		Mo-99/ Sorbent Mass (Ci/g)	Volume (mL)
3.5	40.75	3.77	4	38	32	0.62	123.01	615.8
4	31.20	2.92	3.0	38	31	0.36	125.58	603.2
5	19.97	1.93	2.0	39	32	0.15	120.55	628.3
6	13.87	1.39	1.5	42	35	0.08	111.62	678.6

TABLE 2 Concentration Column Designs for 99% Mo Capture Assuming D∞/Dp = 1

Column ID (cm)	Velocity (cm/min)	$MTZ_{1\%}$ (cm)	Column Length (cm)	Column Volume (mL)	Sorbent Weight (g)	ΔP (atm)	Mo-99/ Sorbent Mass (Ci/g)	Strip Volume (mL)
3.5	40.75	2.733	3	29	24	0.46	164.02	461.8
4	31.20	2.1179	2.5	31	26	0.30	150.69	502.7
5	19.97	1.393	1.5	29	24	0.11	160.74	471.2
6	13.87	0.9999	1.0	28	23	0.05	167.44	452.4

TABLE 3 Concentration Column Designs for 99.9% Mo Capture Assuming $D_\infty/D_p = 3$

Column ID (cm)	Velocity (cm/min)	$MTZ_{0.1\%}$ (cm)	Column Length (cm)	Column Volume (mL)	Sorbent Weight (g)	ΔP (atm)	Mo-99/ Sorbent Mass (Ci/g)	Strip Volume (mL)
3.5	40.75	11.70	12	115	95	1.86	41.00	1847.3
4	31.20	8.99	9.0	113	93	1.07	41.86	1809.6
5	19.97	5.80	6.0	118	97	0.45	40.18	1885.0
6	13.87	4.07	4.3	120	99	0.22	39.40	1922.7

TABLE 4 Concentration Column Designs for 99% Mo Capture Assuming $D_\infty/D_p = 3$

Column ID (cm)	Velocity (cm/min)	$MTZ_{1\%}$ (cm)	Column Length (cm)	Column Volume (mL)	Sorbent Weight (g)	ΔP (atm)	Mo-99/ Sorbent Mass (Ci/g)	Strip Volume (mL)
3.5	40.75	7.96	8	77	63	1.24	61.51	1231.5
4	31.20	6.13	6.3	79	64	0.74	60.28	1256.6
5	19.97	3.99	4.0	79	64	0.30	60.28	1256.6
6	13.87	2.82	3.0	85	70	0.16	55.81	1357.2

Column designs for 99.9% Mo capture assuming $D_\infty/D_p = 1$ are approximately twice as large as those for titania S40 sorbent. Therefore the Mo product volume will be approximately twice as large (~600 mL), assuming that the column is stripped with 16 bed volumes (as in the S40-based process). Column designs assuming $D_\infty/D_p = 3$ for 99.9% Mo capture are respectively larger, resulting in column volumes that are ~120 mL and strip volumes designs that are about 1800 mL.

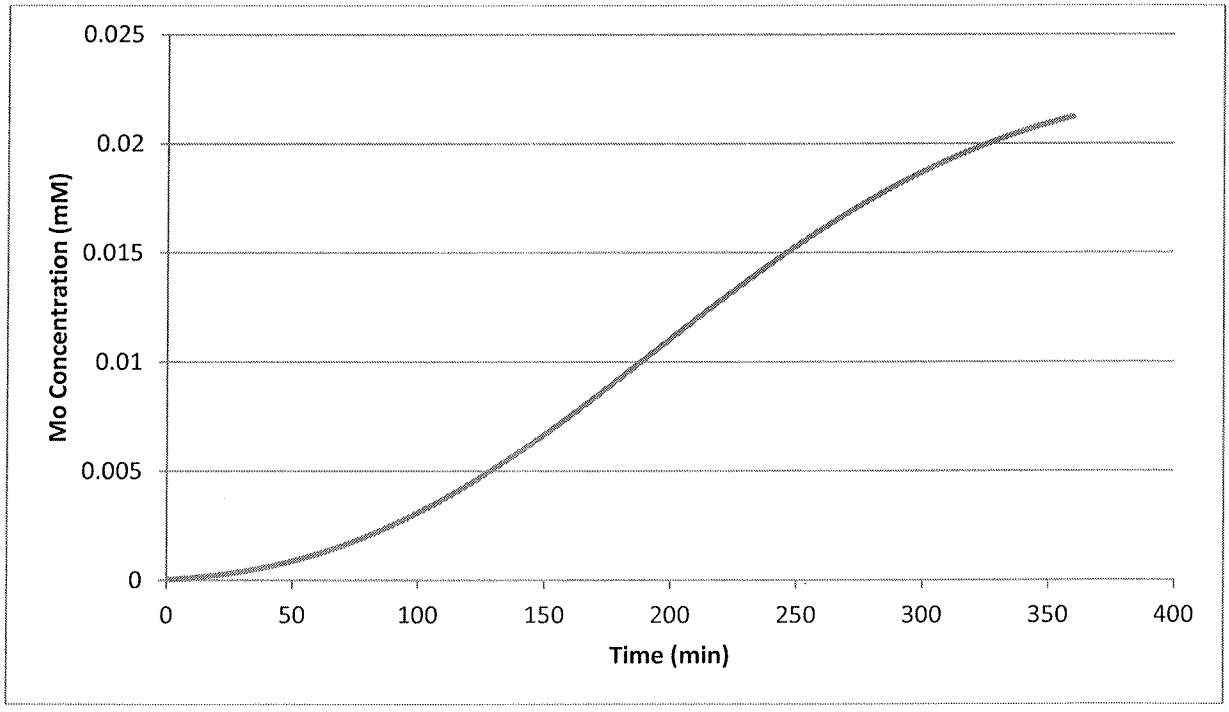

FIGURE 3 Simulated Breakthrough Curve for Loading Mo Solution at 20 cm/min for 360 min on a 0.66 × 1 cm AG 1-X8 Column, Assuming $D_p = D_\infty = 8.3 \times 10^{-4}$ cm²/min.

4 CONCLUSIONS

The results of AG 1-X8 concentration column designs indicate that the column will be at least twice as large as the concentration column utilizing titania S40. This is mainly due to the lower Langmuir adsorption constant for AG 1-X8, a = 5,300, versus S40, a = 22,300 and the larger AG 1-X8 particle diameter (75.5 μm) compared to the S40 particle diameter (40 μm). The larger AG 1-X8 column size is also due to slower Mo intraparticle diffusivity for AG 1-X8, $D_p = D_\infty = 8.3 \times 10^{-4}$ cm^2/min at 25°C, whereas for S40 the process is designed at 80°C and $D_p = 2.34 \times 10^{-3}$ cm^2/min at 80°C. The concentration column design using AG 1-X8 can be improved by loading the feed at higher temperature to increase D_p. Therefore, Langmuir isotherm will be obtained at 50°C (resin thermal stability limit), or other resin forms with higher thermal stability will be considered.

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5 FUTURE WORK

The concentration column designs utilizing AG 1-X8 will be verified by running a column breakthrough experiment with 0.0234 mM Mo in 0.1 M NaOH. The solution will be loaded on a 0.66 × 1 cm AG 1-X8 column at 20 cm/min (6.84 mL) for 360 min (Figure 3). The data will allow verification of intraparticle diffusivity of Mo on AG 1-X8 and verification of mass transfer zone under concentration column loading conditions. The breakthrough experiment assumes that as D_p approaches D_∞, if the $D_\infty/D_p > 1$, then Mo breakthrough will occur sooner.

Once column parameters are verified, a column will be demonstrated in a mini-SHINE experiment (Chemerisov and Vandegrift 2011; Youker et al. 2015) where the behavior of Mo and other fission products will be measured.

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